FIG. 1: Initial magnetization curves of Mn_{12}-acetate at $T = 1.8\,\mathrm{K}$ (black), $T = 2.0\,\mathrm{K}$ (red), and $T = 2.4\,\mathrm{K}$ (green).

the field is faster than at $H_z \neq H_{mm'}$. This picture, first established by magnetic measurements[2], has been confirmed by the careful EPR study of spin levels in Mn_{12}-acetate[8,9,10,11,12,13,14].

The EPR experiments have demonstrated noticeable resonant absorption of electromagnetic radiation by molecular magnets. Most recently, it has been suggested that a crystal of magnetic molecules can also be a powerful source of coherent microwave radiation[15]. The radiation can be produced during the relaxation of the crystal towards the minimum of the magnetic energy. In this paper we provide first experimental support to this suggestion by demonstrating strong interaction between the Mn_{12}-crystal and a microwave cavity. Our intention was to test whether placing the crystal inside a resonant cavity would result in any change in the magnetization curve. Before showing the experimental data, let us discuss why the detection of such an effect would constitute the evidence of the coherent radiation inside the cavity.

Consider a crystal of Mn_{12}-acetate magnetized in the negative Z-direction. At $|H_z| << 10\,\mathrm{T}$ the distance E_1

FIG. 2: Thermally assisted spin tunneling in spin-10 molecular magnets.

between $m = -10$ and $m = -9$ levels in Fig. 2 is about 14 K. Thus, at $T << E_1$, most of the molecules are occupying the $m = -10$ level. The occupation numbers of the excited states scale as $\exp(-E/T)$ where E is the energy distance from $m = -10$. In the absence of a very large transverse field, quantum tunneling from $m = -10$ in Mn_{12} has a negligibly low probability. The thermodynamic equilibrium is achieved either through thermal activation or through thermally assisted quantum tunneling from excited states. The activation of molecules to the excited states is believed to be due to the absorption of phonons. At $T << E_1$ the rate of phonon-induced transitions from $m = -10$ to $m = -9$ for the Hamiltonian of Eq. (1) is given by[16]

$$\Gamma_{phonon} = \frac{\hbar S \omega_1^5}{12\pi\rho c_s^5} \exp\left(-\frac{\hbar\omega_1}{T}\right) , \qquad (3)$$

where $\omega_1 = E_1/\hbar$ is the frequency of the phonon ($f_1 = \omega_1/2\pi \approx 300\,\mathrm{GHz}$), $\rho \sim 1.8\,\mathrm{g/cm^3}$ is the mass density of the crystal, and $c_s \sim 10^5\,\mathrm{cm/s}$ is the speed of the transverse sound. At 2 K Eq. (3) yields $\Gamma_{phonon} \sim 5{\times}10^5 \mathrm{s}^{-1}$.

In order to have any effect due to the electromagnetic radiation, the absorption of photons must have the rate comparable to the rate of the absorption of phonons. This can be achieved in the EPR experiment in which the sample is placed in the ac magnetic field H_{ac} oscillating at frequency f_1. The rate of the absorption of photons in the EPR setup is given by[17]

$$\Gamma_{photon} = k\frac{Sg^2\mu_B^2}{\hbar^2} H_{ac}^2 F(\omega) , \qquad (4)$$

where k is a numerical factor of order one that depends on the polarization of photons and $F(\omega)$ is the shape function of the resonance. In the case of the Lorentzian line of the width $\Delta\omega$, the shape function is given by

$$F(\omega) = \frac{1}{\pi}\frac{\Delta\omega}{(\Delta\omega)^2 + (\omega - \omega_1)^2} . \qquad (5)$$

It reduces to the Delta-function $\delta(\omega - \omega_1)$ for $\Delta\omega \to 0$. At a finite width, the maximal EPR rate is achieved at $\omega = \omega_1$ and is given by $\Gamma_{photon} \sim g\mu_B S H_{ac}^2/\hbar\Delta H$, where ΔH is the field width of the line, $\hbar\Delta\omega = g\mu_B\Delta H$. In Mn_{12}, ΔH is of order of 400 Oe. Consequently, at $H_{ac} \sim 1$ Oe the rate of the absorption of EPR photons becomes comparable to the phonon rate of Eq. (3) and the microwave power delivered to the Mn_{12} crystal can significantly alter the magnetic relaxation.

In our experiments no external ac magnetic field has been used. The crystal of Mn_{12}-acetate was simply placed inside a resonant cavity and the magnetization curve has been measured. Let us assume for the moment that only thermal photons are available for the transitions between, e.g., $m = -10$ and $m = -9$ levels. The wavelength of these photons is comparable to the dimensions of the cavity. Their magnetic field can be then estimated from $H_{ac}^2/8\pi \sim (\hbar\omega_1/V)\exp(-\hbar\omega_1/T)$, where $V \sim 5{\times}10^{-2}\mathrm{cm}^3$ is the volume of the cavity. This gives $H_{ac} \sim 3{\times}10^{-8}$Oe, as compared to $H_{ac} \sim 1$ Oe needed to beat the phonon rate in the EPR experiment at $\Delta H \sim 400$ Oe. Thus at 2 K thermal photons inside the cavity excite Mn_{12} molecules at a rate that is fifteen orders of magnitude lower than the phonon rate. This is mainly due to the fact that at any temperature each cubic centimeter of a solid contains $(c/c_s)^3 \sim 10^{15}$ times more thermal phonons than thermal photons. At $T = 2$ K our cavity would have 10^{-3} average number of thermal photons of energy E_1. Consequently, the cavity should play absolutely no role in the magnetic relaxation unless it occasionally acquires a very large number of non-thermal photons. If all these photons have the same phase, their effect will be equivalent to the effect of the ac magnetic field in the EPR experiment and may become comparable to the effect of the phonons.

Single crystals of Mn_{12}-acetate have been grown with the average length and diameter of about 2 mm and 0.2 mm respectively. The elongation of the crystals was along the c-axis. The conventional composition and the structure of the crystals[18] have been established by chemical, infrared, and X-ray diffraction techniques. In addition, the dc and ac magnetometry of the crystals have been performed. The same values of the blocking temperature and resonance fields, as previously reported[2,19,20], have been found.

In constructing resonant cavities we followed the procedures described in Refs.[21,22]. Five cylindrical cavities of different diameter and adjustable length were constructed using 99.99% purity copper. Two diameters were used: 1.6 mm and 3.2 mm. The length of the cavity was controlled with the help of the same-purity copper rod connected to the upper surface of the cavity. The micrometric stepping motor control system was used that had the spatial resolution of 1 μm. The inner lateral and

FIG. 4: The rate of magnetic relaxation in a Mn_{12}-acetate crystal inside the cavity of diameter 1.6 mm at $T = 2.0$ K as a function of the cavity length at the second (black points) and third (red points) resonance fields.

laxation rate, $\Gamma = |M(H) - M_{eq}(H)|^{-1}(dM/dH)$ (with M_{eq} being equilibrium magnetization), on the length of the cavity at two resonance fields is shown in Fig. 4.

In a separate set of experiments we placed the Mn_{12}-acetate crystal between two Fabry-Perot superconducting mirrors. The mirrors were prepared using method described in Ref.[24]. The 200 nm YBaCuO layers were deposited by pulsed laser deposition on a 1 μm $SrTiO_3$ substrate. Their superconducting properties below 90 K were verified by magnetic measurements. The magnitude of the diamagnetic signal from the mirrors was found to be comparable to the magnitude of the signal from the crystal, but independent from the distance between the mirrors. The demagnetization curves from the Fabry-Perot setup are shown in Fig. 5. The diamagnetic signal from the superconductors was subtracted from the total signal to obtain Fig. 5B. The dependence of dM/dH on the distance between the mirrors at $H_z = 0$ is shown in Fig. 6.

The experimental data clearly demonstrate the dependence of the magnetic relaxation in Mn_{12}-acetate crystals on the geometry of the cavity. We have verified that this phenomenon appears only in cavities of high quality factor. Could it be due to effects unrelated to the electromagnetic properties of the cavity? The first thing that comes to mind is that in the confined geometry the cooling of the crystals by the flow of helium could be not perfect. The rate of thermally assisted quantum tunneling in Mn_{12} depends on temperature exponentially[19]. Thus, fluctuations in the hermetic properties of the cavity could, in principle, result in a significant change of the relaxation rate. For that reason we carefully monitored temperature inside the cavity. The temperature variation was found not to exceed 0.3 %. Such small fluctuations of temperature cannot account for any measurable change in the relaxation rate. All data on the dependence of the rate on the length of the cavity and the magnetic

FIG. 6: dM/dH at $H_z = 0$ and $T = 2.0\,\mathrm{K}$ for a Mn_{12}-acetate crystal between superconducting mirrors as a function of the distance between the mirrors.

cavity, however, a maser effect can take place if some of the frequencies of the emitted photons coincide with resonances of the cavity. The photon emitted by one molecule remains in the cavity and stimulates the emission of photons by other molecules. The shortest wavelength, λ, of a photon corresponds to the transition from $m = 9$ to $m = 10$. For Mn_{12} at $H = 0$ it is about 1 mm. The wavelengths of photons emitted in other transitions are longer. Consequently, for a crystal of size 2 mm, the phase of the emitted photons is the same for a macroscopically large number of molecules, $N = N_{SR} \sim (\lambda/2)^3$. In that case the emission of photons by different molecules becomes correlated and the superradiance may occur[15,23]: The rate of the emission of a photon increases by a factor N_{SR}. This effect is much stronger for photons than for phonons because the wavelength of photons is (c/c_s) times the wavelength of phonons of the same energy. Thus, the $(c_s/c)^3$ smallness of the phase space of photons in comparison with the phase space of phonons is compensated by the $(c/c_s)^3$ times greater N_{SR} for photons as compared to phonons. Crystals used in our experiments contained about $1.6{\times}10^{16}$ Mn_{12} molecules, so that each magnetization step in Fig. 3 and Fig. 5 involved more than 10^{15} molecules. For $Q \sim 3{\times}10^3$ the 300-Ghz photons stay inside the cavity during $t \sim 10\,\mathrm{ns}$. The reabsorption of the radiation by the crystal requires $\Gamma_{photon} t > 1$. According to Eq. (4), our picture is self-consistent if during the 10 s field sweep across the tunneling resonance of width $\Delta H \sim 400\,\mathrm{Oe}$ the cavity was affecting the magnetic relaxation through $10^3(\Delta H/\Delta h)$ microbursts of superradiance of duration 10 ns or less, each burst involving $10^{12}(\Delta h/\Delta H)$ molecules whose resonances were distributed within $\Delta h < 1\,\mathrm{Oe}$.

The effect of $10^{12}(\Delta h/\Delta H)$ coherent photons inside the cavity would be similar to the effect of the 1 Oe ac magnetic field in the EPR experiment. That is, the absorption of the photons increases the population of the levels with $m > -10$ in Fig. 2 as compared to their ther-

mal population. Contrary to the EPR experiment, however, in our case the photons absorbed in the left well in Fig. 2 must be the same photons that are emitted in the right well. One can think about this process as the recycling of the emitted photons by the crystal after the number of photons in the cavity reaches the critical value. To affect the magnetic relaxation, one of the frequencies, ω, of the emitted photons should satisfy two conditions. The first condition is that $\hbar\omega$ coincides with one of the distances between the spin levels in the metastable well (the left staircase in Fig. 2). It is fulfilled for certain values of the field $H_z = H_r$ which are uniquely determined by the spin Hamiltonian. If A in Eq. (1) was zero, the fields H_r would coincide with $H_{mm'}(A = 0) = H_n = nD/g\mu_B$. Because of $A \neq 0$, however, H_r are different from $H_{mm'}$ of Eq. (2), except for $H_z = 0$. Nevertheless, due to the fact that $A << D$, the fields H_r must group around H_n. The second condition is that the resonant frequency corresponding to $H_z = H_r$ also coincides with one of the resonances of the cavity. It is achieved by manipulating the length of the cylindrical cavity or the distance between superconducting mirrors in the Fabry-Perot setup.

Strong support to the above picture comes from the fact that the main period of oscillations of the relaxation rate on the distance between superconducting mirrors, (see Fig. 6) is about 0.5 mm, which is one-half of the wavelength of the 300 Ghz photons responsible for the transitions between $m = -10$ and $m = -9$ levels. This resonance is the most important one because almost all molecules initially occupy the $m = -10$ state. Exciting these molecules to the $m = -9$ level alone changes the effective energy barrier by $E_1 \approx 14\,\mathrm{K}$, thus increasing the relaxation rate by a factor $\exp(E_1/T) \sim 10^3$. For cavities, the length-dependence of the relaxation rate is more complicated. Photons emitted in the magnetic dipole transitions should be in resonance with the TM modes of the cavity. The latter, for a cavity of radius R and length L, satisfy

$$\omega_{mnp}^2 = \frac{c^2\kappa_{mn}^2}{R^2} + \frac{\pi^2 c^2 p^2}{L^2}\ , \qquad (6)$$

where $p = 1, 2, 3, ...$ and $x = \kappa_{mn}$ is the n-th zero of the Bessel function $J_m(x)$. Matching the spectrum of the spin levels of Mn_{12}-acetate with the spectrum of the cavity should be the way to explain the dependence of the magnetic relaxation on the length of the cavity. We have not succeeded in that task so far. Both spectra are rather dense. Their comparison is complicated by the distribution of energy levels due to dipolar and hyperfine fields, crystal imperfections, etc.

The main message that we want to disseminate is that the magnetic relaxation of molecular nanomagnets inside a resonant cavity differs from the magnetic relaxation outside the cavity. It seems impossible to understand this effect without invoking the superradiance. Our findings open the possibility of building a microwave laser pumped by the magnetic field. Measurements of microwave radiation from cavities containing crystals of molecular nanomagnets should be the next step in this direction.

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[1] E. M. Chudnovsky and J. Tejada, *Macroscopic Quantum Tunneling of the Magnetic Moment*, Cambridge University Press, Cambridge - England, 1998.

[2] J. R. Friedman, M. P. Sarachik, J. Tejada, and R. Ziolo, Phys. Rev. Lett. **76**, 3830 (1996).

[3] R. Sessoli, D. Gatteschi, A. Caneschi, and M. A. Novak, Nature (London) **365**, 141 (1993).

[4] J. L. van Hemmen and A. Sütő, Europhys. Lett. **1**, 481 (1986); Physica **B141**, 37 (1986); G. Sharf, W. F. Wreszinski, and J. L. van Hemmen, J. Phys. **A20**, 4309 (1987).

[5] M. Enz and R. Schilling, J. Phys. **C19**, L711 (1986).

[6] E. M. Chudnovsky, Zh. Eksp. Teor. Fiz. **77**, 2158 (1979) [Sov. Phys. JETP **50**, 1035 (1979)]; E. M. Chudnovsky and L. Gunther, Phys. Rev. Lett. **60**, 661 (1988).

[7] D. A. Garanin, J. Phys. **A24**, L61 (1991).

[8] A. L. Barra, D. Gatteschi, and R. Sessoli, Phys. Rev. **B56**, 8192 (1997).

[9] S. Hill, J. A. A. J. Perenboom, N. S. Dalal, T. Hathaway, T. Stalcup, and J. S. Brooks, Phys. Rev. Lett. **80**, 2453 (1998).

[10] E. del Barco, J. M. Hernandez, J. Tejada, N. Biskup, R. Achey, I. Rutel, N. Dalal, and J. Brooks, Phys. Rev. **B62**, 3018 (2000).

[11] A. B. Sushkov, B. R. Jones, J. L. Musfeldt, Y. J. Wang, R. M. Achey, and N. S. Dalal, Phys. Rev. **B63**, 214408 (2001).

[12] B. Parks, J. Loomis, E. Rumberger, D. N. Hendrickson, and G. Christou, Phys. Rev. **B64**, 184426 (2001).

[13] K. Park, M. A. Novotny, N. S. Dalal, S. Hill, and P. A. Rikvold, J. Appl. Phys. **91**, 7167 (2002).

[14] M. Dressel, B. Gorshunov, K. Rajagopal, S. Vongtragool, and A. A. Mukhin, submitted to Phys. Rev. **B**.

[15] E. M. Chudnovsky and D. A. Garanin, Phys. Rev. Lett., in print.

[16] D. A. Garanin and E. M. Chudnovsky, Phys. Rev. **B56**, 11102 (1997); E. M. Chudnovsky and X. Martinez-Hidalgo, Phys. Rev. **B**, in print.

[17] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Clarendon Press, Oxford - England, 1970.

[18] T. Lis, Acta Crystallogr. Sect. **B36**, 2042 (1980).

[19] J. M. Hernandez, X. X. Zhang, F. Luis, J. Bartolomé, J. Tejada, and R. Ziolo, Europhys. Lett. **35**, 301 (1996).

[20] L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, and B. Barbara, Nature (London) **383**, 145 (1996).

[21] M. Mola, S. Hill, P. Goy, and M. Gross, Review of Scientific

Instruments **71**, 186 (2000).

[22] O. Klein, S. Donovan, M. Dressel, and G. Grüner, Int. J. of Infrared and Millimeter Waves **14**, 2423 (1993); S. Donovan, O. Klein, M. Dressel, K. Holezer, G. Grüner, Int. J. of Infrared and Millimeter Waves **14**, 2459 (1993); M. Dressel, O. Klein, S. Donovan, and G. Grüner, Int. J. of Infrared and Millimeter Waves **14**, 2489 (1993).

[23] See reviews: M. Gross and S. Haroche, Phys. Rep. **93**, 301 (1982); L. I. Menshikov, Sov. Physics - Uspekhi **42**, 107 (1999).

[24] A. Garcia-Santiago, F. Sánchez, M. Varela, and J. Tejada, Appl. Phys. Lett. **77**, 2900 (2000).